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HYDROLYTIC STABILITY OF URETHAN ELASTOMERS

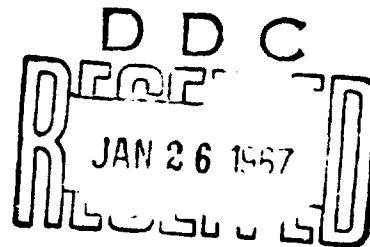


TECHNICAL REPORT

By

Z. T. Ossefort and F. B. Testroet

December 1966



U. S. ARMY WEAPONS COMMAND

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HYDROLYTIC STABILITY OF URETHAN ELASTOMERS*

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INTRODUCTION

Urethan elastomers offer a combination of properties making them attractive for military applications. Among these are high strength, excellent tear, abrasion, oil, ozone, and oxidation resistance and good impact resistance at low temperatures. These properties have been used to advantage in a wide variety of mechanical rubber items, a few of which are pictured in Figure 1.

Many of these items have exhibited complete breakdown after short periods of service in this country and abroad (Figure 2). The rubber loses all of its strength and elasticity and resembles tar.

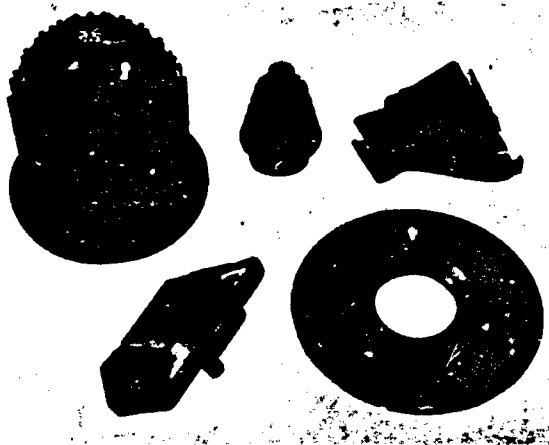


FIG. 1.—Urethan end items. (1) Accumulator bladder—Hawk missile. (2) Bellows—pop up target mech. (3) Butt plate—M60 machine gun. (4) Tank track pad—M113 vehicle. (5) Obturator pad—8" howitzer

In view of these occurrences, an investigation was made to ascertain the cause and develop means for preventing such failures in the future. It was found that the elastomers involved were invariably polyester urethans and exposure conditions often involved high humidity. These observations, coupled with the well recognized susceptibility of esters to hydrolysis, seemed to indicate that failures were due to poor hydrolytic stability. A search of the literature, including manufacturers'

* Presented at a meeting of the Division of Rubber Chemistry, American Chemical Society, San Francisco, California, May 3-6, 1966. H. The opinions or assertions contained herein are not to be construed as official or reflecting the views of the Department of the Army.

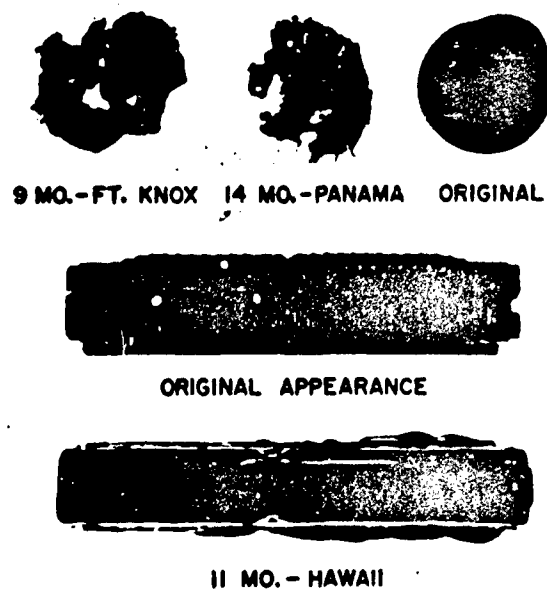


FIG. 2.—Deterioration of urethan items in service. Bellows and machine gun forearm assembly.

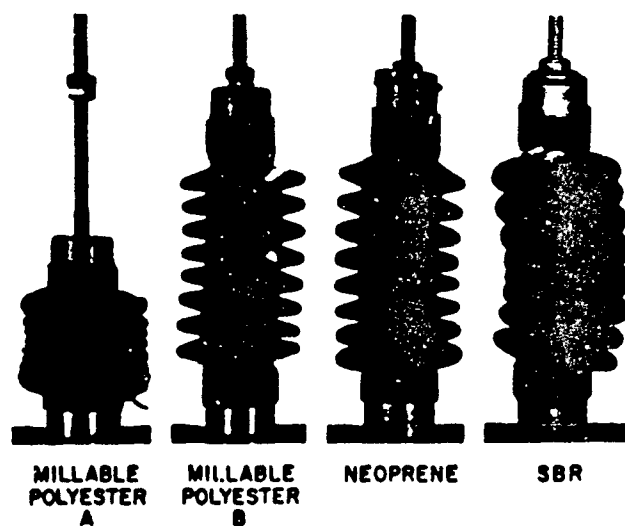


FIG. 3.—Bellows after 14 months outdoors in Panama.

TABLE I
FORMULATIONS AND PROPERTIES OF BELLOWS TESTED AT PANAMA*

Compounding Ingredients	Millable Polyester A	Millable Polyester B	Neoprene ^a	SBR ^c
	Parts by Weight			
Elastomer	100	100	100	100
Stearic acid	0.2	0.2		2
Zinc oxide			5	3
Cumyl peroxide, 40% active	4	4		
FEF black	30	25		50
ISAF black			40	
A blend of selected waxes			3	1
Magnesium oxide			4	
Dioctyl sebacate			35	
Toluene diisocyanate dimer		4		
2-mercaptoimidazoline			1	
Diphenyl-p-phenylenediamine/phenyl- β - naphthylamine, 35/65			3	
Trimethyl dihydroquinoline				1
Phenyl- β -naphthylamine				1
Sulfur				1.75
N-cyclohexyl-2-benzothiazole sulfenamide				1
N,N'-di-3 (5 methyl heptyl)-paraphenylene- diamine				3
Pads compression molded, minutes at °F.	30/320	30/320	30/307	30/307
Stress-Strain Properties				
Tensile strength, psi	3890	4290	2380	2600
Modulus at 300% E, psi	1600	2000	1540	1520
Elongation, %	635	510	385	560
Hardness, Shore A	63	70	51	62

* Outdoor exposure data at Panama are reported on these same compounds in Figure 16.

^b Neoprene WD, E. I. du Pont de Nemours, Inc.

^c SBR 1500.

data, revealed that although numerous references to hydrolytic stability could be found, actual data were scant. That which was found covered relatively short exposure periods or related to urethan foams¹. More recently the water resistance of castable polyester and polyether urethan elastomers has been compared².

In order to determine if field failures could be reproduced in a controlled test, bellows were exposed at Fort Amador in the Canal Zone. Their condition after fourteen months is shown in Figure 3. One of the polyester urethan compounds showed the same type of degradation as found in service. A second containing diisocyanate as a compounding ingredient held up except for cracks at the maximum stress area reminiscent of ozone cracking. (Cracks visible to the naked eye were reported after three months). The neoprene and SBR showed no visual evidence of deterioration. Bent loop specimens (Figure 4) exposed 1 year at Panama and 28 days in a humidity cabinet also exhibited hydrolytically induced cracking. The same compound showed no cracks after 6 months in an ozone cabinet and 4 years outdoors at Rock Island Arsenal and Alaska. (The latter specimens are still in

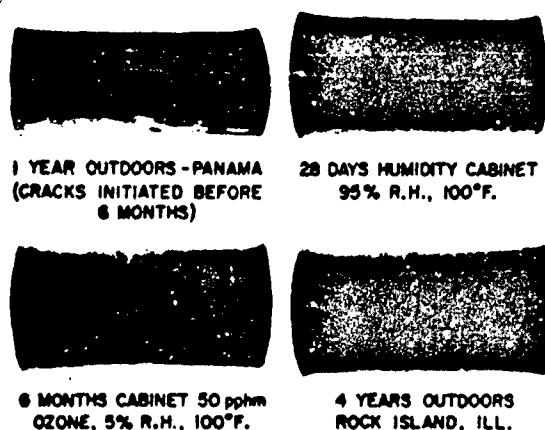


Fig. 4.—Hydrolytic cracking of millable polyester urethane B.

test). Formulations and properties of these compounds are given in Table I. A second set of bellows (with only Polyester A) has been shelf aged at the Rock Island Arsenal Laboratory for 36 months. Again the polyester urethane showed marked deterioration while the other elastomers are still in excellent condition.

Concurrent efforts at reproducing these failures in the laboratory revealed that exposure over water in closed containers for short periods at 158° F caused polyester urethans to revert to a tarlike mass (Figure 5). It was also found that exposure of stressed or unstressed specimens over water in a closed desiccator at room temperature or in a cabinet at 95 per cent R.H. and 100° F resulted in cracking as typified by the examples in Figure 6.

The effects of exposure under the above two conditions on the properties of many millable, castable, and injection moldable polyester and polyether urethans

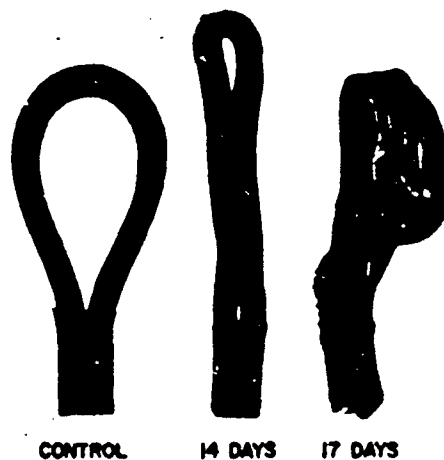


Fig. 5.—Millable polyester urethane A exposed over water at 158° F.

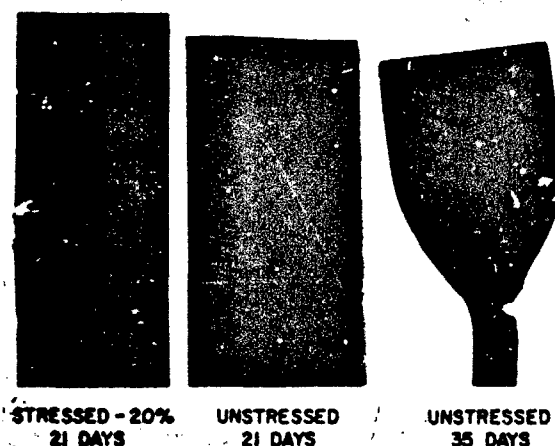


FIG. 6. —Millable polyester A exposed at 95% RH and 100° F.

will be covered in this paper. Emphasis has been on millable types since they were of most interest in our applications. Most commercial urethan elastomers are prepared by the polyaddition polymerization of diisocyanates and hydroxyl terminated polyesters or polyethers. The polyesters are generally prepared by reacting a slight excess of ethylene, propylene, or butylene glycols (or mixtures thereof) with adipic acid². Notable exceptions are those based on castor oil or the more recently introduced caprolactone polymers^{4,5}. The polyether urethans are most frequently prepared from polyether diols such as polyoxytetramethylene glycol obtained by polymerization of tetrahydrofuran.

HYDROLYTIC STABILITY AT ELEVATED TEMPERATURES

A few examples typifying the degradation resulting when cured dumbbell specimens are exposed over or immersed in distilled water at 158° F or 212° F will be presented. Samples from millable gums were prepared from stock mixed on a standard rubber mill per ASTM D15-64T. Pads from the castable urethans were prepared using manufacturers recommendations. A Mini-Jector 1½ ounce injection molding press was used to prepare samples from the thermoplastic urethans. In some cases, cured pads were obtained from suppliers. Testing was done per applicable ASTM methods.

In contrast to oxidative aging, in which tensile strength frequently behaves erratically, this property was an excellent measure of deterioration in these exposures and will be used in the graphical presentation of data. Other properties (except modulus) did not vary as regularly as tensile. Elongation *generally* increased with exposure time but in some cases it remained close to original or decreased. Hardness most frequently decreased but in some cases it stayed near original value. In one extreme case, for example, a 90 durometer compound went from 4800 psi tensile to 1160 psi after 4 weeks over water at 158° F and the hardness was still 90. The volume of the rubber changed only slightly with exposure. In a typical case volume swell after 3 days at 155° F was 4 per cent (tensile 3580 psi). After fourteen days the volume had increased to only 14 per cent while the tensile had dropped to 740 psi.

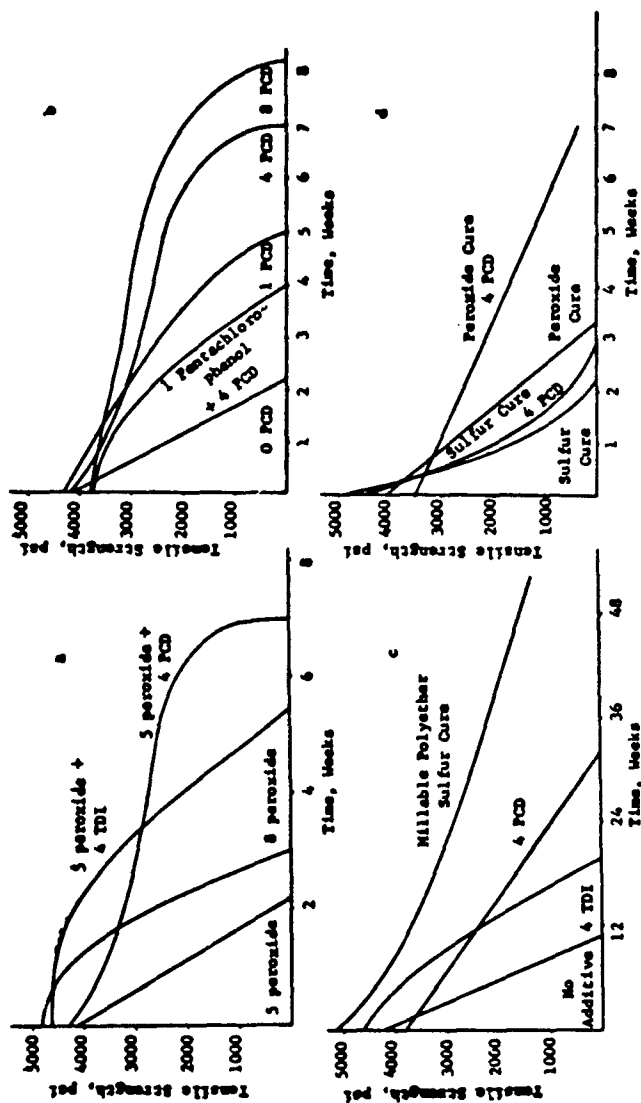


Fig. 7.—Tensile strength of millable urethan compositions as a function of time stored over water at 158° F. a. Millable polyester A, peroxide cured, with additives: polycarbodiimide and diisocyanate; b. Millable polyester A with various amounts of PCD and with pentachlorophenol; c. Millable polyester B with TDI and with PCD and millable polyether urethan sulfur cured; d. Millable polyester C, sulfur and peroxide cured, with and without PCD.

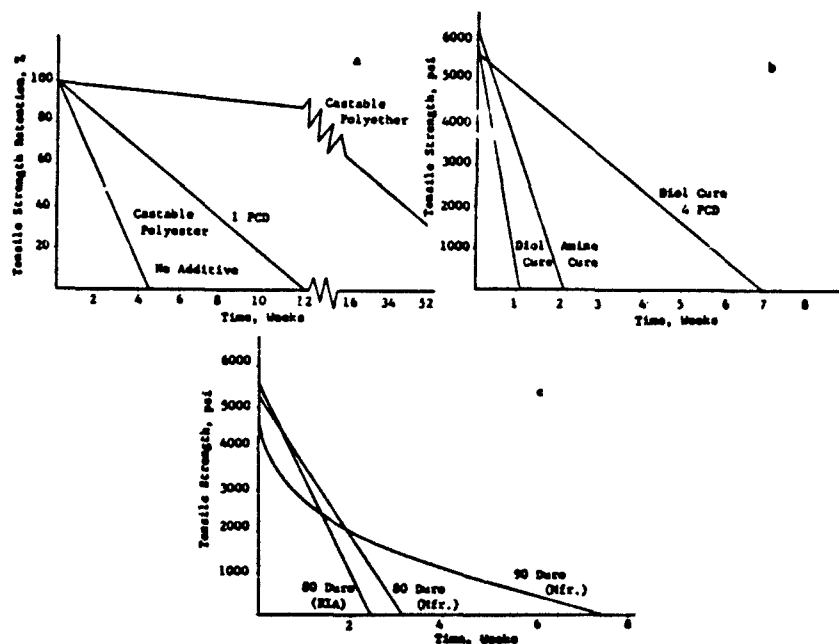


FIG. 8.—Tensile strength or tensile strength retention of castable urethan compositions as a function of time stored over water at 158° F. a. Castable polyester A and a castable polyether. b. Castable polyester B, diol and amine cured, with PCD. c. Castable polyesters based on polylactone diols.

One of the prime objectives of our work was to develop inhibitors to prolong the useful life of the rubber under hydrolytic exposures. To this end 145 additives or combinations which might improve resistance to hydrolysis have been tested. Only a few of these are effective, and, as we shall see, those which give improvement at elevated temperatures frequently lead to accelerated decomposition near ambient temperatures and *vice versa*. Many also produce undesirable effects on the original properties such as lower strength and increased compression set. The performance of two of the most effective of these additives is illustrated in Figure 7a. Polycarbodiimides (PCD) have been found to be most useful in this connection. Stabilization is attributed to the specific reactivity of carbodiimides with free carboxyl groups which catalyze degradation of the polymer. Polycarbodiimides are non-volatile, difficult to extract and have low toxicity. The —N=C=N— bond is relatively inert in polymerization reactions and has little or no reactivity toward sulfur, peroxides, or isocyanates⁸. Polycarbodiimides may be prepared by the condensation polymerization in bulk of diisocyanates at temperatures in the 563° to 580° F range⁷. Many monomeric carbodiimides were tested but none gave as good protection as the polymers. These materials have been described in recent patents^{8,9}. Use of a higher curative level (40 per cent active cumyl peroxide-DCP) yields only slight improvement. Since the ester groups in the main chains are the principal point of attack, it is not surprising that the deterioration is almost independent of crosslink density. Other curing systems tried such as sulfur, diisocyanate, and gamma radiation offered no improvement. Toluene diisocyanate dimer (TDI) when used in conjunction with a peroxide cure provides significant improvement.

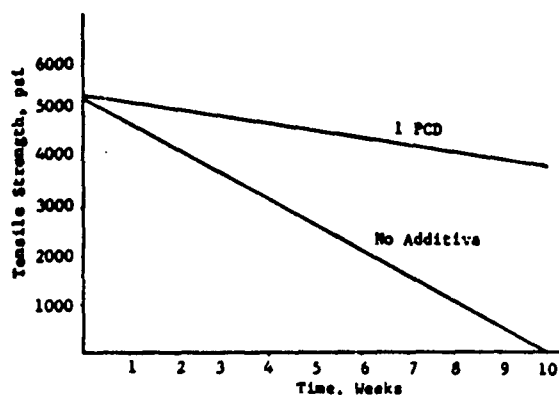


FIG. 9.—Tensile strength of injection moldable polyester A as a function of time stored over water at 158° F.

As indicated in Figure 7b, PCD levels as high as eight parts yield increased protection. However, this high level increases compound costs out of proportion to the benefit obtained. The combination of fungicide (pentachlorophenol) and PCD has poorer stability than PCD alone.

Data for a more hydrolytically stable polyester and a polyether are given in Figure 7c. Both PCD and TDI bring about improvement. However, even with these additives, the polyester is not comparable to the polyether.

In Figure 7d the resistance of sulfur and peroxide cured polyester based vulcanizates with and without PCD are shown. It is unfortunate that the PCD does not significantly improve the stability of the sulfur cured compound since, as we shall see, this compound is one of the most stable in the ambient temperature test.

Typical results obtained on a castable polyester and polyether are presented in Figure 8a. The polyester samples were received from the supplier as cured pads. The value of small quantities of PCD in the polyester is evident but even with this additive it does not approach the stability shown by the polyether.

Castable urethan elastomers are most frequently cured with amines or diols (with suitable catalysts to accelerate the isocyanate-diol reaction; a combination of these may be used). Figure 8b compares the hydrolytic stability of the amine cure and a diol cure with and without PCD. One might expect the diol cure to hold up better in view of the greater hydrolytic stability of a urethan *versus* urea group. However, it appears that the main chain ester groups are hydrolyzing at such a rapid rate that this difference is obscured.

Recently, polyester urethans based on diols obtained through the polymerization of caprolactones have been described⁴. These were reported as having improved hydrolytic stability in comparison with the polyadipate ester diols commonly used although data on water resistance was meager. The data shown in Figure 8c indicate that these polylactone based urethans break down quite rapidly. Samples tested were prepared from the prepolymer in our laboratory using a diamine (MOCA) cure and also obtained from the supplier as cured pads.

Results obtained on injection molded samples furnished by the supplier are given in Figure 9. The value of PCD in this compound is at once apparent. These results again indicate that primary crosslinks do not lead to improved hydrolytic stability. These thermoplastics which are not crosslinked display as much or more resistance to hydrolysis as the covalently crosslinked polyester types we have just seen.

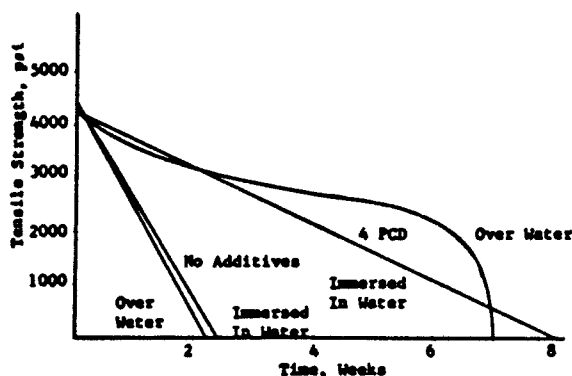


FIG. 10.—Tensile strength of millable polyester A as a function of time immersed in or stored over water at 158° F.

The data furnished in Figure 10 indicate that immersion in water at 158° F produces about the same effect as exposure over water. The latter condition was used more frequently in our work because of its greater similarity to service conditions.

Immersion in water at 212° F is an extremely severe condition for urethan elastomers and leads to rapid deterioration of both polyesters and polyethers as shown in Figure 11. It is apparent that at this temperature not only ester groups are readily attacked but also other hydrolyzable groups present *viz.* urethan, urea, biuret, and allophanate. It is interesting to note that the millable polyether was significantly more resistant than the castable polyether under this very severe condition. This suggests that even under these conditions the main chain ether (and urethan) groups are comparatively stable—rapid breakdown of the castable polyether being due to rupture of the hydrolysis susceptible crosslinks (mainly amide) and greater resistance of the millable attributed to the stability of the crosslinks resulting from the peroxide cure. It has been suggested² that this test may be useful for distinguishing polyether from polyester urethans. However, since the polyester containing PCD showed greater resistance than the castable polyether the test would not be definitive. The color test described by Bauman and Steingiser¹⁰

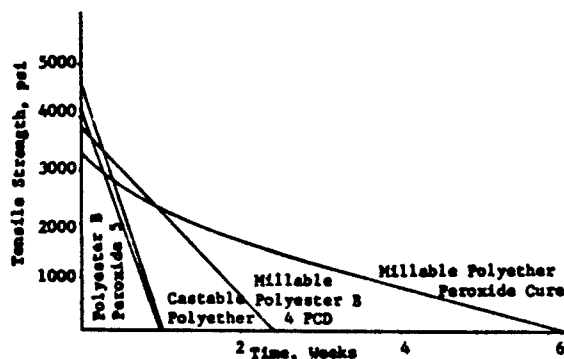


FIG. 11.—Tensile strength of urethan elastomers as a function of time immersed in water at 212° F

is useful in this connection. However, the castable polyester based on polylactone diols gave a negative response. Apparently upon hydrolysis this polyester reverts to the lactone thereby obviating formation of the hydroxamic acid necessary for the color response.

HYDROLYTIC STABILITY AT OR NEAR ROOM TEMPERATURE

The hydrolytic decomposition of polyester urethan elastomers in high humidity at or near room temperature manifests itself in two principal ways. The first, as we have seen, is the short term catastrophic cracking which occurs both in the presence and absence of stress. The second is a gradual softening, over a period of months, and involves those elastomers which show the early cracking as well as "crack resistant" types. The attack is complicated by its association with fungus.

This phase of our work consisted primarily in the exposure of dumbbell or bent loop specimens over distilled water, 0.1N HCl or NH_4OH in a closed desiccator at room temperature or in a humidity cabinet at 95 per cent R.H. and 100° F. Samples were also immersed in water at room temperature. Physical properties were determined periodically on the dumbbell specimens and the time to crack initiation noted for the stressed specimens.

The times to first appearance of cracking for a few of the compounds tested are shown in Figure 12. Owing very likely to the microbiological factor, these times may vary up to a week and occasionally longer on replicate specimens. The polyethers are resistant to hydrolytic cracking. Among the polyesters those based on a

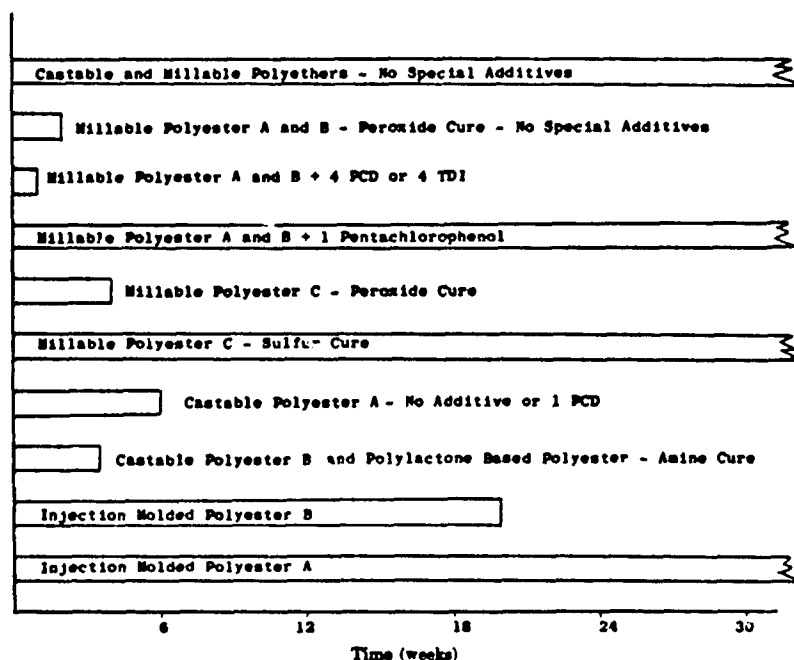


Fig. 12.—Time to first cracking of urethan elastomer specimens exposed to 95% R.H. at 100° F. Injection molded polyethers did not crack.

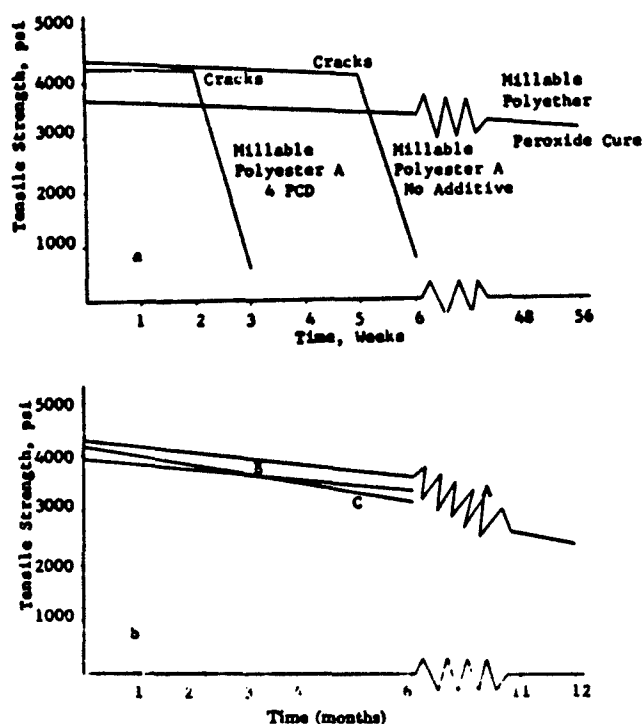


FIG. 13.—Tensile strength of millable polyester urethan elastomers as a function of exposure to water or water vapor at room temperature. a. Millable polyester A over water; b. Millable polyesters immersed in water, all peroxide cures; A and B 5 phr peroxide.

sulfur cure or containing fungicide resist cracking. Of the many fungicides tested pentachlorophenol was the only one which effectively prevented cracking and did not seriously modify the properties of the vulcanizates. It should be noted that Polyester B, one of the most resistant to breakdown at 158° F cracks rapidly under these conditions with or without PCD or diisocyanate. The injection molded samples show good resistance to cracking.

In Figure 13a the strength of polyester and polyether urethans after exposure over water at room temperature is depicted. The polyether has excellent property retention for over a year. The polyesters display rapid breakdown. The PCD which inhibits deterioration at 158° F accelerates the failure under this condition. Specimens were observed to be badly cracked and crazed near the point in time at which tensile dropped rapidly.

Immersion in water at room temperature produces results which are entirely different as shown in Figure 13b. In this case no cracking is noted and tensile strength is observed to drop off very gradually for periods up to over a year.

It appeared from these data that the rapid cracking might be initiated by fungus. In order to determine whether this was the case samples were exposed over water under sterile conditions, over 0.1N HCl and N₂L₄OH, and immersed in water. No cracking was observed in bent loop specimens for periods of over one year under these conditions. However, a gradual softening and loss of strength is observed as illustrated by the tensile data for exposure over 0.1N HCl (Figure 14). The

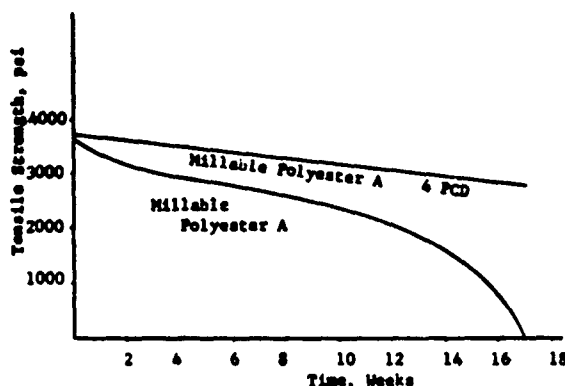


Fig. 14.—Tensile strength of polyester A with and without PCD as a function of time stored over 0.1N HCl at 100° F.

PCD is effective in retarding softening and tensile loss in this case similar to its behavior at 158° F.

In addition to the above, several miscellaneous factors which might have an effect on hydrolytic stability have been investigated using millable polyesters. These included use of carbon black fillers at various levels and in pH range from 5 to 9, mineral fillers, presence or absence of zinc oxide, various peroxide curatives, DCP without the calcium carbonate carrier and various stearic acid levels. None of these had a significant effect on hydrolytic stability as measured by the above tests.

EVIDENCE FOR FUNGUS ASSOCIATION

The evidence that fungi (and possibly other microorganisms) are associated with the deterioration (especially the early cracking) experienced by polyester urethans exposed to high humidity at or near room temperature is abundant. This evidence is direct and indirect and may be summarized as follows:

1. Visible growths during accelerated testing at room temperature—most commonly at the focal point of failure. These are observed whether samples are specifically inoculated with fungi or not. A typical example of such growth (not inoculated) is shown in Figure 15.
2. Specific action of fungicides in preventing the early cracking of stressed or unstressed samples.
3. Resistance of sulfur cured polyesters to cracking—sulfur apparently behaving in this case as a fungicide.
4. Lack of cracking after lengthy exposures over water under sterile conditions.
5. Increased resistance to cracking of specimens immersed in water in comparison with over water.
6. Resistance to cracking when exposed over 0.1N HCl or NH_4OH —such conditions might normally be expected to *accelerate* hydrolytic deterioration rather than retard it. These conditions inhibit growth of fungi.
7. Visible evidence of fungi and mildew odor on degraded items returned from field use.
8. Temperature range of cracking—cracking is observed after short exposure periods at 50° F, 80° F, and 100° F, but at or above 120° F (the temperature near which fungi are inactive) cracking is not observed".

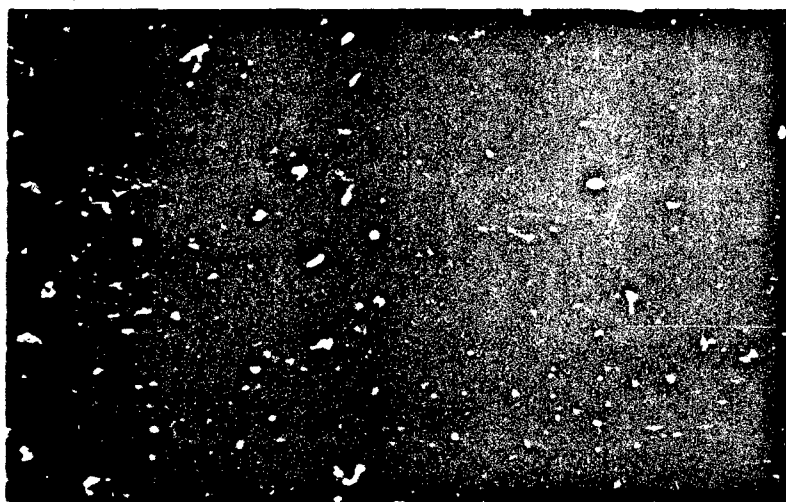


FIG. 15.—Surface of millable polyester A after 28 days exposure over water at 80° F (45X).

The mere fact that microorganisms are observed to grow on the specimens does not necessarily imply degradation of the rubber. Growths were observed on polyether urethans but, as has been shown, these resist deterioration for lengthy periods. On the other hand, it should be emphasized that hydrolytic breakdown occurs at or near room temperature even in the absence of fungal attack (conditions 2, 3, 4 and 6 above). However, this is limited to the progressive softening (and loss of strength) which takes place over a period of many months both in accelerated tests and under tropical exposures. This softening is significantly retarded by hydrolysis stabilizers such as PCD but not by fungicides.

An interesting case was observed with bent loop specimens of Polyester A immersed in water at room temperature. No cracking was noted at 52 weeks. However, at 60 weeks one of the specimens exhibited cracking and a fungus type growth was observed at the point of cracking. The other specimen showed no cracking or microorganisms.

From this evidence it seems clear that microorganisms are associated with the early deterioration of polyester urethans.

OUTDOOR AND SHELF AGING STUDIES

In addition to the accelerated testing just described the effects of outdoor and shelf aging of stressed and unstressed specimens is being investigated. Test pads and bent loop specimens have been exposed under tropical (Panama), arctic (Alaska) and temperate (Illinois) conditions.

The very rapid breakdown of uninhibited Polyester A upon outdoor exposure in Panama is revealed by data in Figure 16a. Fungicide has very little effect in retarding deterioration but PCD is fairly effective. A combination of these agents seems to be useful but original strength is considerably lower. These results correlate well with those obtained in the 158° F test described earlier.

As shown in Figure 16b Polyester B containing no additive is somewhat more resistant to deterioration than Polyester A. Fungicide leads to poorer age resistance in this case. The millable polyether and Polyester B containing TDI are holding

up well thus far. These results again correlate with the 158° F test results. For comparison, data on the aging of unstressed SBR, neoprene, chlorobutyl and EPR at Panama are presented in Figure 16c. As may be seen these compounds hold up quite well under tropical conditions.

Data on test pads exposed at Rock Island, Illinois are given in Figure 17. Degradation at comparable exposure periods is considerably less at this location than at Panama. The value of PCD in Polyester A is apparent. Polyester B containing TDI holds up well indoors but is showing some deterioration outdoors. Results of exposure at Alaska are similar to those obtained at Rock Island.

Stressed specimens of Polyesters A and B showed cracking in periods of less than six months at Panama (cf. Figures 3 and 4) but are crackfree after 51 months in Alaska and at Rock Island.

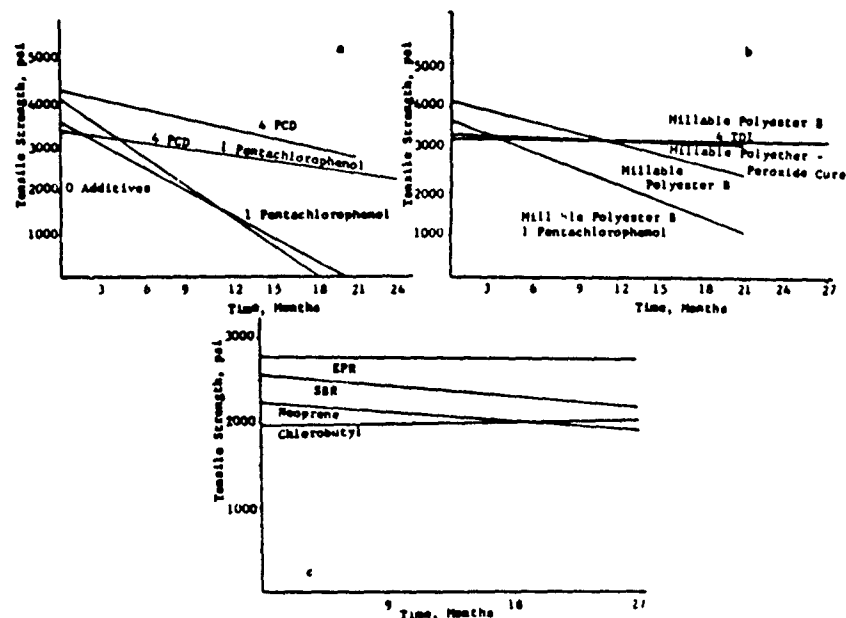


FIG. 16.—Tensile strength of unstressed specimens as a function of time exposed in Panama. a. Millable polyester A with and without additives; b. Millable urethanes; c. Other rubbers.

Results thus far reported have been on thin rubber items (such as the bellows) or test pads in the case of accelerated testing. To ascertain effects of aging in thick sections, dumbbell samples were cut from obturator pad (Item 5—Figure 1) which are approximately one and one half inches thick. Results obtained after various periods of shelf storage at Rock Island on uninhibited and inhibited (PCD) pad are given in Figure 17b. The pad containing PCD has excellent property retention to limit of test (which is continuing). Degradation in the uninhibited pad was uniform throughout the pad's cross section. No cracking has as yet been observed. Tank track pads (Item 4—Figure 1) based on Polyester A (no inhibitor) have been exposed outdoors at Rock Island over weeks. After 24 months fine cracks (readily visible to the naked eye) in most cases, and to the metal back up plates were observed.

TABLE II
FORMULATIONS AND PHYSICAL PROPERTIES OF POLYESTER AND POLYETHER URETHAN VULCANIZATES

	Millable Polyester A						Millable Polyester B					
	5	8	4 TDI	4 PCD	1 PCD	8 PCD	4 PCD & 1	1	5	4 TDI	4 PCD	1
Compounding Ingredients	Peroxide	Peroxide					Penta-chloro-phenol	Penta-chloro-phenol	Peroxide			Penta-chloro-phenol
Elastomer	100	100	100	100	100	100	100	100	100	100	100	100
Stearic acid	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
YFF carbon black	35	35	35	35	35	35	35	35	35	35	35	35
Cumyl peroxide, 40% active	5	5	5	5	5	5	5	5	5	5	5	5
Toluene diisocyanate dimer ^a			4									
PCD ^b				4	1	8	4			4		
Pentachlorophenol							1	1				

Test pads cured 30' at 320° F

Original properties

Tensile strength, psi	4400	4830	4540	4180	4390	3850	3730	3580	4340	4540	3810	2640
Modulus at 300% E, psi	3150		3160	2570	3030	2440	2110	1920	3080	3800	2000	1940
Elongation, %	450	295	440	470	440	515	575	580	380	385	380	600
Hardness, Shore A	71	72	76	68	71	72	70	69	71	82	71	69

^a Multirthane E164, Mobay Chemical Co.

^b Antioxidant PCD Naftane, Inc., 425 Park Ave., N.Y. 22, N.Y. (from Farbenfabriken Bayer, Leverkusen, Germany). Polycarbodiimide 6305/10A, Mobay Chemical Co., Penn Lincoln Parkway West, Pittsburgh, Pa. 15205. Gave equivalent results to "PCD". A PCD prepared by incomplete condensation polymerization of an equimolar mixture of dianisidene and bitolylene diisocyanates gave equivalent results. Time and temperature of reaction should be adjusted to yield a product having a melting point in the 165-185° F range, so that it will be a liquid during processing of the elastomer. For example, with 0.03 moles of each diisocyanate a product melting in this range was obtained after heating 30 minutes at 575° F. The product was pulverized and used without further treatment.

TABLE II (Continued)
 FORMULATIONS AND PHYSICAL PROPERTIES OF POLYESTER AND POLYETHER URETHAN VULCANIZATES

	Milled Polyester C				Castable Polyester A			Castable Polyester B		
	Peroxide cure	Peroxide cure 4 PCD	Sulfur cure	Sulfur cure 4 PCD	No additive	1 PCD	Diol cure 100	Diol cure PCD 100	Amine cure 100	
Elastomer										
Stearic acid	0.2	0.2	0.2	0.2	Received from manufacturer as cured test pads					
SAF black	30	30	30	30						
Cumyl peroxide, 40% active	3	3								
Sulfur			2	2						
2-Mercaptobenzothiazole			2	2						
Benzothiazyl disulfide			4	4						
Zinc chloride complex ^a			1	1	No special additive	Contains 1% PCD				
Calcium stearate			0.5	0.5						
PCD ^b		4		4			6.5	4		
Diol curative ^c							6.5	6.5		9
Methylene bis- <i>s</i> -chloranilins										
N-ethyl morpholine							0.75	0.75		
Tetraethyleneglycol dimethyl ether							2.5	2.5		
A chlorinated plasticizer ^d							2.5	2.5		
Original properties										
Tensile strength, psi	4020	3050	4900	4520	5600	5500	5770	5760	6210	
Modulus at 300% E, psi			2500	1820	2270	2240	800	840	1750	
Elongation, %	290	300	525	585	600	625	805	805	675	
Hardness, Shore A	73	71	80	80	91	93	74	75	87	

Test pads cured 30 min at 320° F.

^a ZC 455 Activator, Thiokol Chemical Corporation.

^b Cyanacryl Curative B, American Cyanamide Company.

^c Aroclor 1260, Monsanto Chemical Company.

TABLE II (Continued)
FORMULATIONS AND PHYSICAL PROPERTIES OF POLYESTER AND POLYETHER URETHAN VULCANIZATES

	Polylactone Based Polyester		Injection Moldable Polyester A		Milleable Polyether		Castable Polyether		Chlorobutyl		EPR ²		Injection Moldable Polyester B
	80 Duro (HIA)	80 Duro (Mfr.)	90 Duro (Mfr.)	No Additive	1 PCD	Sulfur cure	Peroxide cure	Polyether	100	100	100	100	
Elastomer	100	Test pads prepared by manufacturer		Test pads prepared by manufacturer		100	100	100	100	100	100	100	Test pads prepared by manufacturer
Methylene bis- <i>o</i> -chloroaniline	10.6	manufacturer				1.5		12					
Sulfur													
2-Mercaptobenzothiazole													
Benzothiazyl disulfide				No special additives	Contains 1% PCD ³	1							
HAF carbon black						3							
Cumyl peroxide, 40% active						30	30						
Magnesium oxide							2.5						
Stearic acid													
Phenyl- β -naphthylamine													
Process oil													
EPC carbon black													
Zinc oxide													
Calcium stearate													
Tetramethyl thiuram disulfide													
Phenol formaldehyde resin ⁴													
2,2'-methylene-bis(4-methyl-6-tertiary-butyl phenol)													
Original properties	5690	5350	4830	5280	5350	5170	4000	3670	1950	2800	4090		
Tensile strength, psi													
Modulus at 300% E, psi	1980	2000		3030	3280	2180	2410	2350	1310	860	2010		
Elongation, %	410	380	235	505	585	515	420	370	490	670	505		
Hardness, Shore A	80	82	90	96	97	70	68	90	66	60	92		

Test pads cured 30 min at 320° F.

¹ HT1066 supplied by Enjay Chemical Company.

² EPR MD 460 supplied by Enjay Chemical Company.

³ Amberol ST137 supplied by Rohm & Haas.

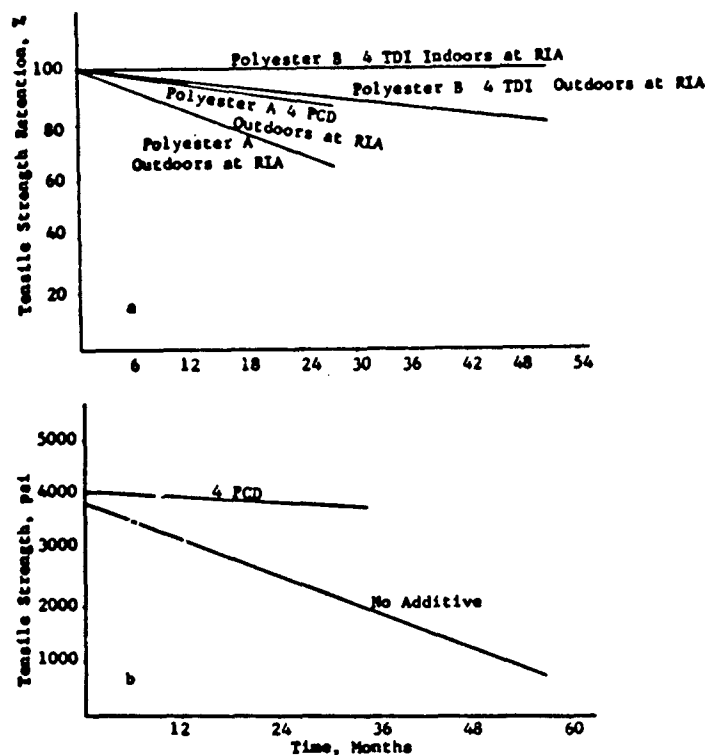


FIG. 17.—Tensile strength or retention of millable polyesters as a function of time stored at Rock Island Arsenal (RIA), Illinois. a. Millable polyesters A and B; b. Millable polyester A samples cut from obturator pads.

These observations and data reveal that thick rubber sections are subject to both reversion and hydrolytic cracking (under high humidity conditions) similar to the thinner materials.

Detailed formulations and original properties of the various polyurethan elastomers utilized in this work are given in Table II. These are identified in the same way as on the various graphs.

SUMMARY AND CONCLUSIONS

Data have been presented bearing on the hydrolytic stability of a wide variety of urethan elastomers (Table III). It has been shown that polyester based elastomers are considerably more susceptible to hydrolytic attack than polyether elastomers up to 158° F. The nature of the attack and results obtained are profoundly influenced by the temperature. At temperatures of 120° F and above the attack appears to be a "simple" hydrolysis consisting of scission of main chain ester groups resulting in reversion of the rubber. In this case aging over water and in water are similar. At temperatures below 120° F the attack cannot be rationally treated without considering the part played by fungi. In this case exposure over water yields drastically different results from immersion—the former being more severe by several orders

TABLE III
DESCRIPTION OF URETHAN ELASTOMERS USED IN THIS STUDY

Trade name	Supplier	Processing type	Chemical type	Cure type
Adiprene B	Du Pont	Millable	Ether	Isocyanate
Adiprene C	Du Pont	Millable	Ether	Sulfur or peroxide
Adiprene L	Du Pont	Castable	Ether	Amine
Castomer A4	Isocyanate Products Co.	Castable	Ester	Amine
Castomer A7	Isocyanate Products Co.	Castable	Ester	Amine
Cyanaprene VG	American Cyanamid	Millable	Ester	Sulfur or peroxide
C ⁿ -anaprene 4509	American Cyanamid	Castable	Ester	Amine or diol
Elastothane 455	Thiokol	Millable	Ester	Sulfur or peroxide
Estane 58105	B. F. Goodrich	Injection moldable	Ester	Thermoplastic
Genthane S	General Tire & Rubber Co.	Millable	Ester	Peroxide
Genthane SR	General Tire & Rubber Co.	Millable	Ester	Peroxide
Multrathane F66	Mobay Chemical Co.	Castable	Ester	Diol
Roylar A-855	U. S. Rubber	Injection moldable	Ester <i>Ether</i>	Thermoplastic
Texin 192A	Mobay Chemical Co.	Injection moldable	Ester	Thermoplastic
Texin 280A	Mobay Chemical Co.	Injection moldable	Ester	Thermoplastic
Texin 480A	Mobay Chemical Co.	Injection moldable	Ester	Thermoplastic
Texin 355D	Mobay Chemical Co.	Injection moldable	Ester	Thermoplastic
Vibrathane 5003	U. S. Rubber	Millable	Ester	Peroxide
Vibrathane 5004	U. S. Rubber	Millable	Ester	Peroxide
Vibrathane 5005	U. S. Rubber	Injection Moldable	Ester	Peroxide
LD387	Du Pont	Injection Moldable	Ether	Thermoplastic
ECD498	Du Pont	Castable (One shot)	Ether	Thermoplastic
PR1689 N*	Wyandotte Chemicals Corp.	Castable (One shot)	Ether	Amine-diol
PR1689 P*	Wyandotte Chemicals Corp.	Castable (One shot)	Ether	Amine-diol

* Experimental products resulting from Contract DA-20-018-ORD-24383.

of magnitude. Typically the attack over water involves a short term (two to three weeks) cracking of stressed or unstressed specimens and a gradual softening which takes place over a period of many months. The cracking seems to be connected with fungus attack.

Resistance of polyesters to hydrolytic attack can be improved by the use of additives such as diisocyanates, fungicides, and carbodiimides. The latter are most useful and apparently scavenge the carboxylic acid resulting from hydrolytic breakdown of the polyesters thereby preventing autocatalysis. Their ability to react with carboxylic acids under these mild conditions has been reported¹². Differences among polyesters not only in inherent resistance to hydrolysis but also in response to inhibition are found. As has been seen the early cracking can be eliminated by use of sulfur cures, or inclusion of a fungicide but only at the expense of reduced resistance at 158° F.

Accelerated tests have been shown to correlate reasonably well with outdoor exposures. Results on unstressed specimens correlate with the 158° F test while the stressed specimens yield results similar to exposure at 95 per cent R.H. and 100° F.

Not all linear polyesters are susceptible to hydrolysis such as is poly(ethylene propylene adipate). The terephthalate polyesters, poly(ethylene terephthalate) and poly(1,4 cyclohexane dicarbonyl terephthalate), have been exposed in the form of thin films over water at 158° F for 14 months and over water at 95 per cent R.H. and 100° F for 23 months without visible signs of deterioration. They are apparently stabilized by the presence of the aromatic rings or steric factors or a combination of these.

In conclusion it must be said that although some progress has been made in protecting polyester urethan elastomers from hydrolytic failure under tropical and high humidity conditions, the problem has only partially been solved.

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13 ABSTRACT The resistance to hydrolysis of millable, castable, and injection moldable urethan elastomers was determined. Conditions most frequently used were exposure over water at 158°F. and at or near room temperature. Polyesters were shown to suffer much more rapid deterioration under both conditions than polyethers. Attack at 158°F. appears to involve a simple hydrolysis of the main chain ester groups resulting in reversion. Attack at or near room temperature is more complex, involving both a rapid (typically two to three weeks) hydrolytic cracking of stressed or unstressed specimens and a gradual reversion over a period of many months. The latter attack (especially the early cracking) seems to be of microbiological origin. Hydrolytic decomposition can be retarded by additives such as diisocyanates, carbodiimides, and fungicides. However, these agents frequently lead to lower original properties. Also, those giving protection at 158°F. often cause accelerated deterioration at or near room temperature while those providing protection at the lower temperatures lead to accelerated deterioration at 158°F. Results of outdoor and shelf aging at Rock Island, Illinois and Panama indicate a general correlation with accelerated tests. (U) (Author)		

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